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(71)Applicant : TOPPAN PRINTING CO LTD

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(72)Inventor : FUKUYOSHI KENZO
KIMURA YUKIHIRO
KOGA OSAMU
IMAYOSHI KOJI

(54) ELECTRODE SUBSTRATE FOR DISPLAY

(57)Abstract:

PROBLEM TO BE SOLVED: To eliminate the deterioration on ageing and to attain preservation stability by using a silver alloy prepared by adding small amts. of gold and copper to silver for an argentine thin film.

SOLUTION: The electrode substrate 15 for a transmission-type display consists essentially of the transparent oxide thin film 11 (oxidic transparent conductive thin film layer) as a conductive adhesive layer, transparent argentine thin film 12 (argentine conductive thin film layer) and transparent oxide thin film 13 (oxidic transparent conductive thin film layer)

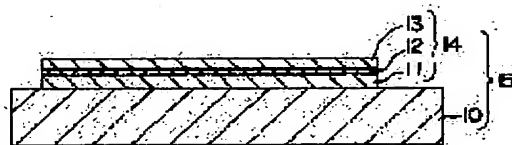
successively formed on a glass substrate 10. In this

case, the argentine conductive thin film layer 12 is formed with a silver alloy added with 0.1-2.5 atomic % gold and 0.3-3.0 atomic % copper, and the oxidic

transparent conductive thin film layer 13 is formed by an amorphous material. The addition of only 0.1 atomic %

gold to the argentine conductive thin film layer 12 in the

substrate 15 is enough to improve the moisture resistance of the conductive adhesive layer 11, argentine conductive thin film layer 12 and oxidic transparent conductive thin film layer 13 as a three-layer conductive film.



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(71) 出願人 000003193

凸版印刷株式会社

東京都台東区台東1丁目5番1号

(72) 発明者 福吉 健蔵

東京都台東区台東1丁目5番1号 凸版印刷株式会社内

(72) 発明者 木村 幸弘

東京都台東区台東1丁目5番1号 凸版印刷株式会社内

(72) 発明者 古賀 修

東京都台東区台東1丁目5番1号 凸版印刷株式会社内

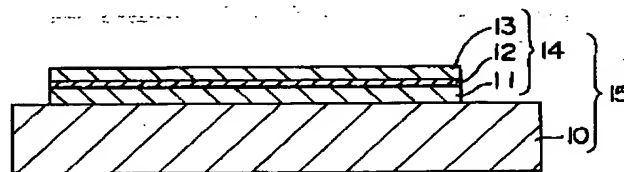
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(54) 【発明の名称】 表示装置用電極基板

(57) 【要約】

【課題】 薄膜で導電性と可視光線透過率又は反射率が高く、しかも経時劣化がなく保存安定性に優れた透過型又は反射型の表示装置用電極基板を提供することにある。

【解決手段】 基板上に導電性接着層と銀系導電薄膜層と酸化物系透明導電薄膜層とをこの順に積層せしめた透過型又は反射型の表示装置用電極基板で、銀系導電薄膜層12が、0.1～2.5at% (atomic weight %) の金、及び0.3～3.0at%の銅を添加した銀合金により形成され、酸化物系透明導電薄膜層13が非晶質物質により形成されている。



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【特許請求の範囲】

【請求項1】基板上に導電性接着層と銀系導電薄膜層と酸化物系透明導電薄膜層とをこの順に積層せしめた電極基板において、銀系導電薄膜層が0.1～2.5at%の金及び0.3～3.0at%の銅を添加した銀合金により形成され、酸化物系透明導電薄膜層が非晶質物質により形成されていることを特徴とする表示装置用電極基板。

【請求項2】前記銀系導電薄膜層の層厚が50～200nmの範囲内にあり、且つ酸化物系透明導電薄膜層の層厚が40～100nmの範囲内にある請求項1記載の表示装置用電極基板。

【請求項3】前記銀系導電薄膜層の層厚が5～25nmの範囲内にあって、前記導電性接着層が、前記酸化物系透明導電薄膜層と同種の酸化物を含有する請求項1記載の表示装置用電極基板。

【請求項4】前記導電性接着層及び酸化物系透明導電薄膜層の全体若しくは一部が、屈折率2.1より大きい酸化物を含有する請求項3記載の表示装置用電極基板。

【請求項5】前記導電性接着層及び酸化物系透明導電薄膜層が、酸化セリウムと酸化チタンのうちいずれか一方若しくは両方より選ばれた酸化物を含有する請求項3又は請求項4記載の表示装置用電極基板。

【請求項6】前記導電性接着層及び酸化物系透明導電薄膜層が、酸化インジウムを含有する請求項3乃至請求項5記載の表示装置用電極基板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、液晶ディスプレイ装置やプラズマディスプレイ装置などの出力表示装置あるいは表示画面から直接入力する入出力用表示装置あるいは太陽電池などに使用される透過型電極（透明電極）や反射型電極の電極基板に関し、特に薄膜で導電性と光線透過率が高く、しかも保存安定性に優れた電極基板に関する。

【0002】

【従来の技術】ガラス、プラスチックフィルムなどの基板上に、可視光線を透過する電極形状の透明導電膜が設けられた電極板は、液晶ディスプレイ装置などの各種表示装置（表示画面）の表示用電極や、この表示装置の表示画面から直接入力できる入出力電極などに広く使用されている。

【0003】例えば、液晶が用いられたディスプレイ装置の透明電極板は、図12に示すように、ガラス基板30と、このガラス基板30上の画素部位に設けられ、画素毎にその透過光を赤、緑、青にそれぞれ着色するカラーフィルタ層31と、上記ガラス基板30上の画素と画素との間（画素間）の部位に設けられ、この部位からの光透過を防止する遮光膜32と、上記カラーフィルタ層31上の全面に設けられた透明保護層33と、この保護

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層33上にスパッタリングにより成膜され、所定の電極パターンにエッチングされたパターン状若しくはベタ状の透明電極34と、この透明電極34上に成膜された配向膜35とでその主要部が構成されている。

【0004】この透明電極34としては、その高い導電性に着目して、酸化インジウム中に酸化錫を添加したITO薄膜が広く利用されており、その比抵抗はおよそ $2.4 \times 10^{-4} \Omega \cdot \text{cm}$ で、透明電極として通常適用される240nmの膜厚の場合、その面積抵抗値は、およそ 10Ω （又は $10 \Omega / \square$ 、 \square ；スクエアと称する）である。また、この他にも酸化錫薄膜や、酸化錫に酸化アンチモンを添加して構成される薄膜（ネサ膜）、あるいは酸化亜鉛に酸化アルミニウムを添加して構成される薄膜などが知られているが、これらはいずれも上記ITO薄膜よりも導電性が劣り、また酸やアルカリに対する耐薬品性あるいは耐水性などが不十分なために一般には普及していない。

【0005】一方、1982年、日本で開催された第7回ICVMにおいて、熱線反射膜として銀薄膜の表裏面にITO薄膜又は酸化インジウム薄膜（IO薄膜）を積層させて構成される3層構造の透明導電膜が提案されている。この3層構造の透明導電膜はおよそ5 Ω 程度の低い面積抵抗値を有しており、その高い導電性を生かして上記透明電極への応用が期待された。

【0006】

【発明が解決しようとする課題】ところで、上記ディスプレイ装置や入出力装置においては、近年、画素密度を増大させて緻密な画面を表示することが求められ、これに伴って上記透明電極パターンの緻密化が要求されており、例えば100 μm 程度のピッチで上記透明電極の端部を構成することが要求されている。また、液晶ディスプレイ装置において基板に液晶駆動用ICが直接接続される方式（COG）においては、配線の引き回しが、幅20～50 μm という細線となる部分があり、従来にない高度のエッチング加工適性と高い導電性（低い抵抗値）が要求されている。

【0007】また、その一方で表示画面の大型化も求められており、このような大型画面化について、上述したような緻密パターンの透明電極を形成し、しかも液晶に十分な駆動電圧を印加できるようにするためには、上記透明電極として面積抵抗値5 Ω 以下という高い導電性を備えた透明電極を適用する必要がある。また、これに加えて、STN液晶等を利用した単純マトリクス駆動方式の液晶表示装置において、16階調以上の多階調表示を行う場合には、3 Ω 以下というさらに低い面積抵抗値が要求されている。

【0008】しかしながら、第7回ICVMにおいて提案された上記3層構造の透明電極においても、高々5 Ω 程度の面積抵抗値が得られるに過ぎず、十分な導電性が確保できないという問題点があり、例えば、銀薄膜の厚

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さを16～18nm程度に厚くすることにより、その面積抵抗値を約3Ωに低下させることは可能であっても、可視光線透過率（特に波長610nm程度の長波長側の可視光線透過率）が75%程度まで低下し、透明電極としての機能が損なわれてしまう。

【0009】さらに、上記3層構造の透明電極においては、銀の薄膜が積層海面などから進入した空気中の水分と反応し易く、その表面に反応物を生成してシミ状の欠陥を生じ、例えば液晶表示装置の透明電極に適用した場合には、その表面に表示欠陥などを生じ易いという問題点があった。

【0010】また、近年、偏光板を用いない、あるいは1枚の偏光板（通常TN型、STN型、ECB型、OCB型などの液晶表示装置では2枚の偏光板を用いる）のみによる反射型液晶表示装置が注目されている。

【0011】加えて、液晶セル内に、光の反射板と表示電極の機能を併せ持たせてコストダウンを図るようにした反射型電極を配設した反射型液晶表示装置の開発が進められている。

【0012】本発明者らは、可視領域のほぼ全域に亘ってアルミニウム薄膜よりも光の反射率の高い銀系薄膜を、反射電極として用いることを提案している。この銀系薄膜は、空気中のイオウ化合物と化合してその表面に硫化物が生成され、反射率が低下し易い問題があり、この銀系薄膜の硫化を防ぐため、銀系薄膜上に透明酸化物の薄膜を積層する方法はきわめて有効である。

【0013】しかし、銀系薄膜上に透明酸化物の薄膜を光学条件を考慮せずに積層すると、反射光が黄色やピンク色に着色して、反射型液晶表示装置の表示品位を大きく落としてしまう問題があった。また、反射電極においても、上述した3層構造の透明電極と同様に、耐湿性が低く、放置しておくだけでも湿気によってシミが発生するという欠点があった。

【0014】本発明は、このような問題点に着目してなされたものであって、その課題とするところは、薄膜で導電性と可視光線透過率又は反射率が高く、しかも経時劣化がなく保存安定性に優れた透過型又は反射型の表示装置用電極基板を提供することにある。

【0015】

【課題を解決するための手段】本発明は、上記課題を解決するための手段として、2つの手法を併用することであり、その1つは、銀系薄膜の銀に少量の金と銅を添加し、銀の性状を抑えることであり、もう1つは、透明酸化物の薄膜を非晶質化し、銀の粒界拡散（銀は酸化物の結晶間での粒界拡散を起こし易い）を無くすことである。

【0016】即ち本発明の請求項1に係る発明は、基板上に導電性接着層と銀系導電薄膜層と酸化物系透明導電薄膜層とをこの順に積層せしめた電極基板において、銀系導電薄膜層が0.1～2.5at%の金及び0.3～

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3.0at%の銅を添加した銀合金により形成され、酸化物系透明導電薄膜層が非晶質物質により形成されていることを特徴とする表示装置用電極基板である。

【0017】また請求項2に係る発明は、上記発明の表示装置用電極基板において、前記銀系導電薄膜層の層厚が50～200nmの範囲内にあり、且つ酸化物系透明導電薄膜層の層厚が40～100nmの範囲内にある表示装置用電極基板である。

【0018】また請求項3に係る発明は、上記発明の表示装置用電極基板において、前記銀系導電薄膜層の層厚が5～25nmの範囲内にあって、前記導電性接着層が前記酸化物系透明導電薄膜層と同種の酸化物を含有する表示装置用電極基板である。

【0019】また請求項4に係る発明は、上記発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層の全体若しくは一部が、屈折率2.1より大きい酸化物を含有する表示装置用電極基板である。

【0020】また請求項5に係る発明は、上記発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層が、酸化セリウムと酸化チタンのうちいずれかが一方若しくは両方より選ばれた酸化物を含有する表示装置用電極基板である。

【0021】また請求項6に係る発明は、上記発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層が、酸化インジウムを含有する表示装置用電極基板である。

【0022】

【発明の実施の形態】本発明の請求項1に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0023】本発明の請求項1に係る発明は、基板上に導電性接着層と銀系導電薄膜層と酸化物系透明導電薄膜層とをこの順に積層せしめた電極基板において、銀系導電薄膜層が0.1～2.5at%（以下atomic weight%、原子量パーセントをat%と称する）の金及び0.3～3.0at%の銅を添加した銀合金により形成され、酸化物系透明導電薄膜層が非晶質物質により形成されている表示装置用電極基板である。

【0024】上記基板上における上記銀系導電薄膜層への金の添加量は、3層構造の導電膜である導電性接着層、銀系導電薄膜層、酸化物系透明導電薄膜層のそれぞれ耐湿性の向上に関しては、0.1at%の少量添加から効力があり、この添加量を多くするに従って耐湿性が向上する傾向がある。

【0025】但し、金の添加量が多くなると導電膜としての抵抗値が上昇し、且つ2.5at%以上とすると導電膜のエッチング加工時に残滓が残り易くなるため、適宜な添加量の調整が必要である。

【0026】銀系導電薄膜層への銅の添加は、上記したように耐湿性向上に寄与するとともに、銀（Ag）の

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み、又はAg-Au（金）の2元素では、スパッタリング成膜時のガス雰囲気中の酸素の影響を受けて成膜厚さや成膜後の透過率などに変動が生じ易いが、銅（Cu）を添加すると凹みが無くなり、従って雰囲気の影響を受け難くなり、特に銀系導電薄膜層の成膜時のマージン（成膜条件などの許容量）を拡げる効力がある。

【0027】具体的には、銀系導電薄膜層の成膜時の導入ガスあるいはバックグラウンドに酸素が多く存在すると、波長470nm付近に光吸収が生じて、透明電極としての光透過率（反射型電極では反射率）の低下が生じる。

【0028】図5は、銀系導電薄膜層が0.1~2.5at%の金及び0at%~3.0at%の銅を添加した銀合金により形成された透明な銀系導電薄膜層と、非晶質物質による酸化物系透明導電薄膜層により形成された3層構造の透明な表示装置用電極基板（3層構造の導電膜の総膜厚；約85nmの場合）の分光透過率を示すグラフであり、グラフ①は銅0at%添加の場合、グラフ②は銅0.3at%添加の場合、グラフ③は銅1.0at%添加の場合、グラフ④は銅3.0at%添加の場合であって、上記銀系導電薄膜層への銅の添加量は、上記図5に示すように、0.3%程度から徐々に短波長側での凹みが減少し、短波長側の透過率の落ち込みを上昇させる効果がある。

【0029】銅は、銀に対して共晶の（完全固溶でない）形をとるため、銅の添加量が多くなると、光透過率若しくは反射率に悪い影響を与えるようになり、また、添加量が多くなると、導電膜の抵抗値が上昇する傾向がある。

【0030】例えば、上記銀系導電薄膜層の膜厚を10~11nmとし、且つ銅の添加量を3at%以上とした場合には、面積抵抗値は5Ωを超えるようになる。

【0031】上記酸化物系透明導電薄膜層を非晶質化するには、ある種の金属酸化物に異種金属を相当量（酸化物の相溶性によって変わるが一般的に20%以上）混合せしめた酸化物ターゲットを用いて、スパッタリングなどの成膜法により基板温度を低く設定して（例えば20℃以下、若しくは室温など）非晶質化することが簡便である。

【0032】また、上記金属酸化物としては、耐酸性や

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耐アルカリ性、耐熱性に富む材料から選定すればよい。

【0033】次に、反射電極の用途を前提として、ガラス基板上に、酸化物系の導電薄膜による導電性の接着層（例えば膜厚10nm、屈折率2.3、但し光波長による屈折率や吸収係数の変化など波長分散を無視した）と、銀系導電薄膜層50nm~200nmと、酸化物系透明導電薄膜層（例えば膜厚40nm）とを順次積層した反射型の表示電極基板のシミュレーションを行った。

【0034】そして、上記反射型の表示電極基板の導電薄膜層の反射率のシミュレーション結果を図11に示す。グラフ①は銀系導電薄膜の膜厚50nm、グラフ②は銀系導電薄膜の膜厚75nm、グラフ③は銀系導電薄膜の膜厚100nm、グラフ④は銀系導電薄膜の膜厚200nmの場合を示す。なお、使用する測定媒質（測定光の経路内に介在する媒質）の屈折率を1.5とした。

【0035】次に、本発明の請求項2に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0036】請求項2に係る発明は、上記請求項1の発明の表示装置用電極基板において、前記銀系導電薄膜層の層厚が50~200nmの範囲内にあり、且つ酸化物系透明導電薄膜層の層厚が40~100nmの範囲内にある表示装置用電極基板である。

【0037】即ち、請求項2に係る発明は、反射型表示電極基板の用途を前提として、反射層としての銀系導電薄膜層の膜厚が50nm~200nmの範囲内にあり、且つ酸化物系透明導電薄膜層の膜厚が40nm~100nmの範囲にあるものである。

【0038】図11は、銀系導電薄膜層の膜厚の反射率に対する影響を示すものであるが、銀系導電薄膜層の膜厚が50nmを超えると、反射率80%前後の反射型電極となり、200nmでは反射率が飽和して、光透過率はほぼ0%となることが示されている。

【0039】図8及び図9に、反射型電極における各々銀系導電薄膜層の膜厚と反射率との関係について、その波長分散を考慮したシミュレーション結果を示し、表1に、各々銀系導電薄膜層（AgAuCu）と酸化物系導電薄膜層（ICTTO）について、その光学定数（屈折率、光の消衰係数）を示した。

【0040】

【表1】

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波長 (nm)	AgAuCu		ICTTO	
	屈折率	消衰係数	屈折率	消衰係数
400	0.1730	1.9500	2.4986	0.0444
410	0.1729	2.0714	2.4736	0.0347
420	0.1666	2.1820	2.4510	0.0275
430	0.1594	2.2835	2.4304	0.0220
440	0.1575	2.3750	2.4116	0.0178
450	0.1510	2.4715	2.3944	0.0145
460	0.1434	2.5674	2.3787	0.0120
470	0.1365	2.6588	2.3643	0.0099
480	0.1316	2.7467	2.3510	0.0083
490	0.1306	2.8313	2.3387	0.0070
500	0.1300	2.9186	2.3274	0.0059
510	0.1299	3.0107	2.3169	0.0051
520	0.1298	3.0979	2.3072	0.0044
530	0.1293	3.1784	2.2981	0.0038
540	0.1286	3.2576	2.2897	0.0033
550	0.1248	3.3404	2.2818	0.0029
560	0.1212	3.4213	2.2745	0.0025
570	0.1202	3.5013	2.2676	0.0022
580	0.1206	3.5800	2.2612	0.0020
590	0.1210	3.6570	2.2551	0.0017
600	0.1243	3.7330	2.2495	0.0016
610	0.1277	3.8076	2.2441	0.0014
620	0.1310	3.8809	2.2391	0.0013
630	0.1338	3.9654	2.2344	0.0011
640	0.1366	4.0481	2.2299	0.0010
650	0.1393	4.1292	2.2256	0.0009
660	0.1400	4.2109	2.2216	0.0008
670	0.1399	4.2918	2.2178	0.0008
680	0.1399	4.3713	2.2142	0.0007
690	0.1402	4.4492	2.2108	0.0006
700	0.1423	4.5250	2.2076	0.0006

【0041】上記酸化物系透明導電薄膜層の膜厚が30 nm以下及び110 nm以上で、435 nm（青色の主波長）の反射率が約70%と低くなることが示されている。

【0042】また、酸化物系透明導電薄膜層の膜厚が、40 nm～100 nmの範囲では良好な反射率をもつことが示されている。

【0043】次に、本発明の請求項3に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0044】請求項3に係る発明は、上記請求項1に係る発明の表示装置用電極基板において、前記銀系導電薄膜層の層厚が5～25 nmの範囲内にあって、前記導電性接着層が前記酸化物系透明導電薄膜層と同種の酸化物を含有する表示装置用電極基板である。

【0045】図10に、透過型電極の用途を前提として、ガラス基板上に、酸化物系の透明導電薄膜による導電性の接着層（例えば膜厚35 nm、屈折率2.2）と、銀系導電薄膜層15 nm～25 nmと、酸化物系透明導電薄膜層（例えば膜厚40 nm）とを順次積層した透過型の表示電極基板による分光透過率のシミュレーション

を示した。グラフ①は銀系導電薄膜層の膜厚15 nm、グラフ②は銀系導電薄膜層の膜厚17.5 nm、グラフ③は銀系導電薄膜層の膜厚20.0 nm、グラフ④は銀系導電薄膜層の膜厚22.5 nm、⑤は銀系導電薄膜層の膜厚25.0 nmの場合であり、測定媒質はエア（空気）として屈折率1とした。

【0046】銀系導電薄膜層の膜厚が25 nmの比較的に厚い領域でも、ピークの透過率は、比較的良好な80%が得られる。また、銀系導電薄膜層の膜厚は20 nm強で、3層構造の導電膜の面積抵抗値は、約2Ωとなる。

【0047】また、銀系導電薄膜層は、膜厚5 nm未満ではアイランド状（ランド状）になり、均質な膜とはならず、計算上での適正な光学特性や抵抗値を算出することが困難となり、また、膜厚5 nm以下の極薄膜の領域では、良好な3層の導電膜とはならない。

【0048】加えて、透過型の表示電極基板を前提とした3層構造の導電膜は、銀系導電薄膜層の表裏両面側に積層されているそれぞれ酸化物系透明導電薄膜層の成膜状態（例えば、成膜時の条件、酸素分圧など）が互いにより近似している方が、透過率と抵抗値に良い影響を与

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える。

【0049】また、銀系導電薄膜層の表裏両面側のそれぞれ前記酸化物系透明導電薄膜層の成膜材料が同じであれば、スパッタリング成膜用のターゲットなど材料管理も容易である。

【0050】ところで近年、STNやECBなど単純マトリクス方式の液晶ディスプレイ表示装置の技術進歩は著しく、CRT代替のモニターとしてカラーSTN方式を使おうという動きがあり、据え置きモニターの場合、100V、110Vといった外部電源との接続が可能であり、こうしたことから高輝度のバックライトの常用が可能となる。

【0051】この観点からモニター用途の単純マトリクス方式の液晶ディスプレイ表示装置では、これに用いる透明電極は低抵抗値であることを優先して、透過率をある程度犠牲にして良いことになるが、このような単純マトリクス方式では、画質向上にとっては透明電極の抵抗値の影響がきわめて大きいし、前述した透明電極の面積抵抗値が2Ω付近になると、シャドウイングと称される画質の低下がほとんど無くなるため、ディスプレイとして実用レベルでTFT方式と競合できる。

【0052】次に、本発明の請求項4に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0053】請求項4に係る発明は、上記請求項3に係る発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層の全体若しくは一部が、屈折率2.1より大きい酸化物を含有する表示装置用電極基板である。

【0054】本発明者らは、さらに検討を重ねたところ、上記のように、酸化物系透明導電薄膜層に屈折率が2.1より大きい酸化物を用いた3層構造の導電膜の構成が、さらに良好な結果を得ることを見出した。

【0055】そして、屈折率の高い酸化物（可視光領域で透明であれば酸化物に限定するものではないが製造コスト等の点で酸化物が実用的である）を、接着層あるいは酸化物系透明導電薄膜層の全体、若しくはこれらの一部に挿入することにより、光透過率の向上に効果があることを見出した。

【0056】高屈折率材料を用いての光透過率のアップは、エアー（空気）よりも屈折率の高い液晶材料（通常液晶の屈折率は1.5～1.6程度）や、カラーフィルタ（カラーフィルタの材料の屈折率は1.5を若干超える程度）と接する形態の液晶表示装置を対象とした3層構造の導電膜の場合に顕著である。

【0057】例えばガラス等の基板上に形成された3層構造の透過型の表示電極の片側がエアー（空気）である場合のシミュレーション結果を図6のB線で示すが、透過率Tはピークで96%程度、反射率Rは1%に近いところまで下がり、透過型の表示電極基板（透明電極）としての良好な結果が得られる。

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【0058】ここでは基板側の透明酸化物薄膜による接着層の膜厚を40nm、透明な銀系導電薄膜層（Ag薄膜）の膜厚を14nm、空気と接する側の酸化物系透明導電薄膜層（透明酸化物薄膜）の膜厚を44nmとした。そして、それら透明酸化物薄膜の屈折率をITOとほぼ同じ2.0として算出した。

【0059】しかし、3層構造の上記透明電極上にポリイミドの配向膜を40nm積層し、これに接する液晶の屈折率を1.5として算出すると、図6のA線で示すように透過率Tはピークが90%以下に低下し、反射率Rは光波長550nm付近でおよそ10%まで上昇して、透過型の表示電極基板（透明電極）としての性能が低下してしまう。

【0060】本発明者らは、このことから3層構造の透過型の表示電極基板に液晶の配向膜としてのポリイミド膜と液晶が接する形での計算を、銀系導電薄膜層をその表裏で挟むそれぞれ透明な酸化物薄膜の各々屈折率を変えて（屈折率を変えると同時に膜厚も調整して）最適化して行った。

【0061】その結果を図6に示す。この図から、透明酸化物薄膜の屈折率が特に2.1を超える程度に高い方が透過率が向上し、また反射率も低下することがわかる。

【0062】次に、本発明の請求項5に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0063】請求項5に係る発明は、上記請求項3又は請求項4に係る発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層が、酸化セリウムと酸化チタンのうちいずれか一方若しくは両方より選ばれた酸化物を含有する表示装置用電極基板である。

【0064】透過型の表示電極基板（透明電極）を前提とした場合、本発明に用いる透明酸化物薄膜に用いて材料としては、高屈折率材料を用いることにより透過率を向上せしめるものである。

【0065】この高屈折率材料の代表的な酸化物は、酸化セリウムと酸化チタンであり、これらを、およそ20～80%の割合で異種酸化物と混合して、透明な導電性の接着層及び酸化物系透明導電薄膜層を形成することにより、透明電極としての3層構造の導電膜の光透過率を向上させるものである。

【0066】次に、本発明の請求項6に係る発明を、実施の形態にしたがって以下に詳細に説明する。

【0067】請求項6に係る発明は、上記請求項3又は請求項4又は請求項5に係る発明の表示装置用電極基板において、前記導電性接着層及び酸化物系透明導電薄膜層が酸化インジウムを含有する表示装置用電極基板である。

【0068】本発明の表示装置用電極基板においては、表示素子の駆動のために、電気的導通を透明酸化物薄膜

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の表面からとる必要がある。

【0069】また透明酸化物薄膜を、熱的にも比較的安定した形（例えば250℃付近のアニールでも結晶化が進まないような形）で非晶質化させるためには、前記したようにおよそ20～80%の範囲で異種酸化物添加の混合酸化物薄膜にする必要がある。

【0070】こうした非晶質の混合酸化物の状態で電気的な導通がとれる酸化物は少なく、本発明者らの検討した範囲では、透明酸化物薄膜の材料を酸化インジウムとすることが有利であることを見出した。

【0071】さらに具体的には、酸化インジウムと、酸化セリウム（あるいは酸化チタン）を、およそ20～80%の範囲で混合せしめた酸化物ターゲットを用いてスパッタリングなどの成膜方法で成膜すればよい。なお、混合割合は、上記した範囲に入らなくても透明酸化物薄膜として非晶質であればよい。

【0072】本発明の表示装置用電極基板は、透過型又は反射型の表示装置用電極基板のいずれをも包含するのであるが、例えば、反射型の表示装置用電極基板である場合は、用いる基板は、ガラス、プラスチックなどの透明な基板、又は白、黒、その他の色に着色された透明又は不透明な基板であってもよい。そして、基板の材料も、ガラス、プラスチックフィルム、プラスチックシート、セラミック、金属板、あるいはアモルファスシリコン、ポリシリコン、MIMなどの半導体素子が形成された基板など種々のものが使用できる。また、用いる前記基板には、予めカラーフィルタ層（例えばレッド、グリーン、ブルーの各着色層）をパターン形成してあってもよい。

【0073】また、本発明の3層構造の導電膜は低抵抗値であるため、TFTやMIMなどの素子の信号線やバスラインなどに使用でき、これらの画素電極と兼用することも可能である。

【0074】

【実施例】以下に本発明の具体的実施例を示す。

【0075】＜実施例1＞図1に示すように、この実施例に係る透過型の表示装置用電極基板15は、厚さ0.7mmのガラス基板10上に順次積層された厚さ35nmの導電性の接着層である透明酸化物薄膜11（酸化物系透明導電薄膜層）と、厚さ14nmの透明な銀系導電薄膜12（銀系導電薄膜層）、及び厚さ38nmの透明酸化物薄膜13（酸化物系透明導電薄膜層）とで、その主要部が構成されている。なお、上記透明酸化物薄膜11、13は、そのいずれもが酸化セリウム（酸素を除く金属元素換算で32at%）を、酸化インジウムの薄膜に加えた混合酸化物とした。また、上記透明酸化物薄膜11、13間の銀系薄膜12は、銀に、金1.0at%と銅1.5at%とを添加した銀合金である。

【0076】そして、上記3層構造の透明導電膜14は、以下のような方法で成膜した。まず、ガラス基板1

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0の表面を有機アルカリ系の界面活性剤と水とで洗浄した後、真空槽内に収容し、逆スパッタリングと称されるプラズマ処理を施し、さらに表面を洗浄処理した。

【0077】次に、ガラス基板10を真空槽中から取り出すことなく、このガラス基板10を室温に維持した状態で、スパッタリング法により透明酸化物薄膜11、銀薄膜12及び透明酸化物薄膜13を順次積層成膜した。

【0078】次に、透明酸化物薄膜13上に電極形状のレジスト膜をフォトリソグラフィ法にてパターン形成し、このレジスト膜から露出した部位を硝酸系エッチング液によりエッチングして、上記3層構造の薄膜を互いに位置整合させた状態で電極形状にパターンニングし、続いて、220℃、1時間のアニール処理を施して、電極形状の上記透明電極14を形成して、透過型の表示装置用電極基板15を作製した。こうして得られた透明電極14の面積抵抗値は、約3.3Ωであった。

【0079】図4に、上記膜厚14nmの銀系導電薄膜層を施した実施例1の透明電極14の可視光線透過率

（グラフ①）を実線にて示す。なお、グラフ②は膜厚12nm以下の銀系導電薄膜層を施した透明電極14（面積抵抗値；約4.6Ω）の透過率、グラフ③は膜厚19nmの銀系導電薄膜層を施した透明電極14（膜厚；約90nm、面積抵抗値；約2.2Ω）の透過率を示す。

【0080】このパターン形成した透明電極14を60℃、湿度95%の雰囲気内に、500時間保持した後、その表面を観察した。その結果、その表面は何ら外観変化を生じなかった。なお、この混合酸化物による透明電極14の屈折率を測定したところ、2.24であった。

【0081】この透明電極14を、薄膜X線回折でその結晶性を調べたところ、銀薄膜12による微小の銀のピークは観察されたものの、透明酸化物薄膜11、13による結晶のピークは観察されなかった。

【0082】そして、上記透明電極14は、熱的にも安定で、300℃まで熱処理しても、透明酸化物薄膜に結晶のピークは観察されず、その面積抵抗値の上昇もほとんど見られなかった。

【0083】＜実施例2＞図2に示すように、この実施例に係る反射型の表示装置用電極基板25は、厚さ0.5mmのガラス基板20上に、順次積層された導電性の接着層である厚さ10nmの酸化物薄膜21（透明乃至不透明酸化物薄膜）と、厚さ150nmの銀系薄膜22（銀系導電薄膜層）と、厚さ75nmの透明酸化物薄膜23（酸化物系透明導電薄膜層）とで、その主要部が構成されている。

【0084】上記透明酸化物薄膜21、23は、酸化インジウム、酸化セリウム、酸化錫、酸化チタンを、各々酸素原子を数に含めない金属原子のみのアトミックパーセントにて、インジウム66at%、セリウム32.5at%、錫1.0at%、チタン0.5at%の組成とした。これら3層構造の反射導電膜24の面積抵抗値は

(8)

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約0.2Ωであった。

【0085】この反射型の表示装置用電極基板25の分光特性を図3に示すが、400nmで80%、450nm～700nmでは、ほぼ90%以上の高い反射率が得られた。

【0086】そして、上記3層構造の反射導電膜24は、以下のような方法で成膜した。まず、ガラス基板20の表面を有機アルカリ系の界面活性剤と水とで洗浄した後、真空槽内に収容し、逆スパッタリングと称されるプラズマ処理を施し、さらに表面を洗浄処理した。

【0087】次に、ガラス基板20を真空槽中から取り出すことなく、このガラス基板20を室温に維持した状態で、スパッタリング法により透明酸化物薄膜21、銀薄膜22及び透明酸化物薄膜23を順次積層成膜した。

【0088】次に、透明酸化物薄膜23上に電極形状のレジスト膜をフォトリソグラフィ法にてパターン形成し、このレジスト膜から露出した部位を硝酸系エッチング液によりエッチングして、上記3層構造の薄膜を互いに位置整合させた状態で電極形状にパターンニングし、続いて、220℃、1時間のアニール処理を施して、電極形状の上記反射導電膜24を形成して、反射型の表示装置用電極基板25を作製した。こうして得られた反射導電膜24の面積抵抗値は、約0.2Ωであった。

【0089】反射導電膜24を薄膜X線回折で結晶性を調べたところ、銀薄膜22による銀の結晶ピークは観察されたものの、透明酸化物薄膜21、23による結晶のピークは観察されなかった。

【0090】反射導電膜24は、熱的にも安定で、300℃まで熱処理しても透明酸化物薄膜21、23による結晶のピークは観察されなかった。また、60℃、湿度95%の雰囲気内に500時間保持して、その表面を観察した結果、外観変化もなく耐湿性の高いものであった。

【0091】

【発明の効果】本発明の表示装置用電極基板は、銀に少量の金と銅を添加した銀合金を銀系薄膜に用いることにより、また同時に透明酸化物薄膜を非晶質とすることにより、表示装置用電極基板に耐湿性を付与でき、信頼性を高くする効果があり、また、屈折率2.1以上の高屈折率の透明酸化物薄膜を用いることにより、透過率の高い透過型の表示装置用電極基板が得られ、可視光の波長全域に亘って反射率の高い反射型の表示装置用電極基板が得られる効果があり、薄膜で低抵抗値であって良好な導電性を示すとともに、可視光線透過率又は反射率が高く、しかも経時劣化がなく保存安定性に優れた透過型又は反射型の表示装置用電極基板として実用的効果がある。

【図面の簡単な説明】

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【図1】本発明の透過型の表示装置用電極基板の側断面図。

【図2】本発明の反射型の表示装置用電極基板の側断面図。

【図3】本発明の反射型の表示装置用電極基板の分光反射率を示すグラフ。

【図4】本発明の透過型の表示装置用電極基板の分光透過率を示すグラフ。

【図5】本発明の透過型の表示装置用電極基板における銀系導電薄膜への銅の添加量率とその時の分光透過率との関係を示すグラフ。

【図6】屈折率2の透明な酸化物系導電薄膜を用いた透過型の表示装置用電極基板において、測定媒質の屈折率が1.0の場合のシミュレーションによる分光透過率Tと分光反射率Rを示すグラフBと、測定媒質の屈折率が1.5の場合のシミュレーションによる分光透過率Tと分光反射率Rを示すグラフA。

【図7】本発明の透過型の表示装置用電極基板において、透明な酸化物系導電薄膜の各種の屈折率(2.0～2.4)と透過率との関係を示すグラフ。

【図8】本発明の反射型の表示電極基板における各々銀系導電薄膜層上の酸化物系透明導電薄膜層の膜厚(30nm～60nm)と、その分光反射率のシミュレーション結果を示すグラフ。

【図9】本発明の反射型の表示電極基板における各々銀系導電薄膜層上の酸化物系透明導電薄膜層の膜厚(70nm～110nm)と、その分光反射率のシミュレーション結果を示すグラフ。

【図10】本発明の透過型の表示電極基板の銀系導電薄膜の膜厚と透過率(反射率)とのシミュレーション結果による関係を示すグラフ。

【図11】本発明の反射型の表示電極基板の銀系導電薄膜の膜厚と反射率とのシミュレーション結果による関係を示すグラフ。

【図12】従来の液晶ディスプレイ装置の透過型の表示電極基板の側断面図。

【符号の説明】

10…基板 11…透明な導電性の接着層 12…銀系透明導電薄膜層

13…酸化物系透明導電薄膜層 14…透明導電膜 15…透過型表示電極基板

20…基板 21…導電性の接着層 22…銀系導電薄膜層

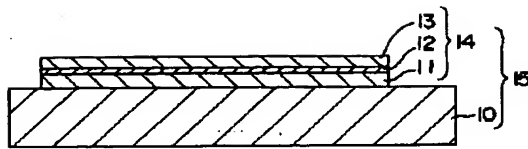
23…酸化物系透明導電薄膜層 24…反射導電膜 25…反射型表示電極基板

30…基板 31…カラーフィルタ層 32…遮光膜層

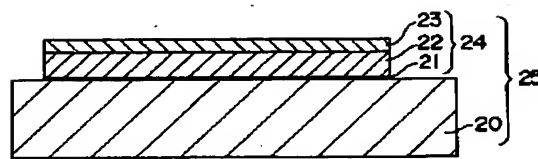
33…透明保護層 34…透明導電層 35…配向膜層

(9)

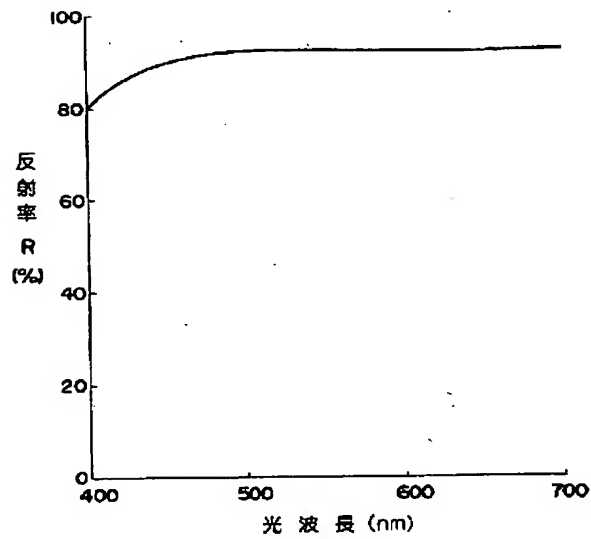
【図1】



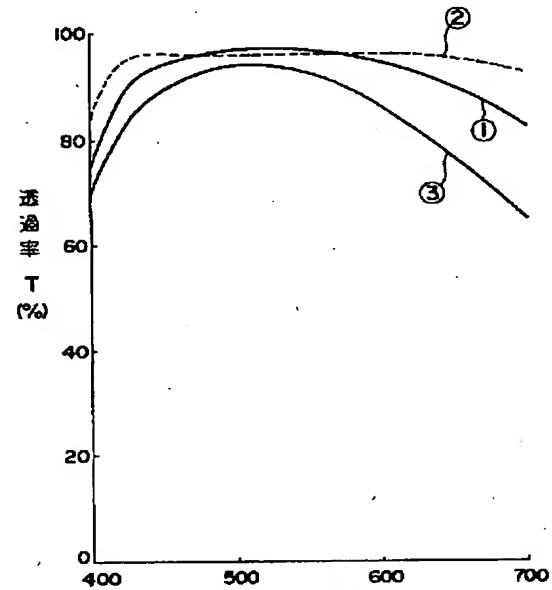
【図2】



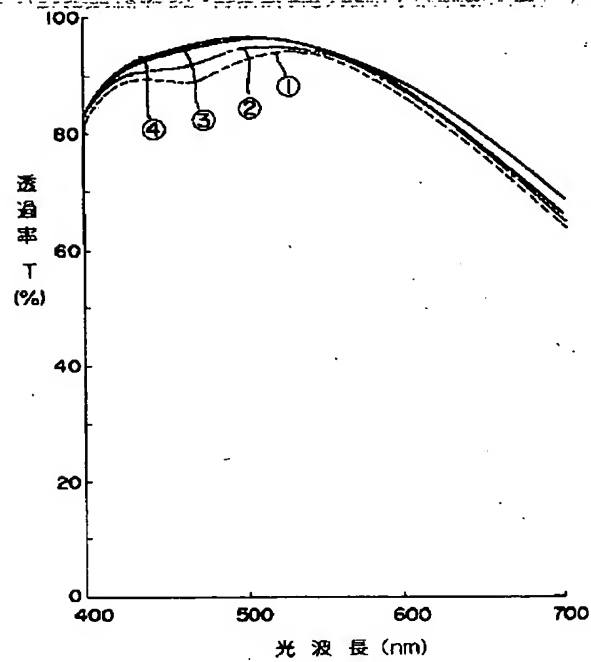
【図3】



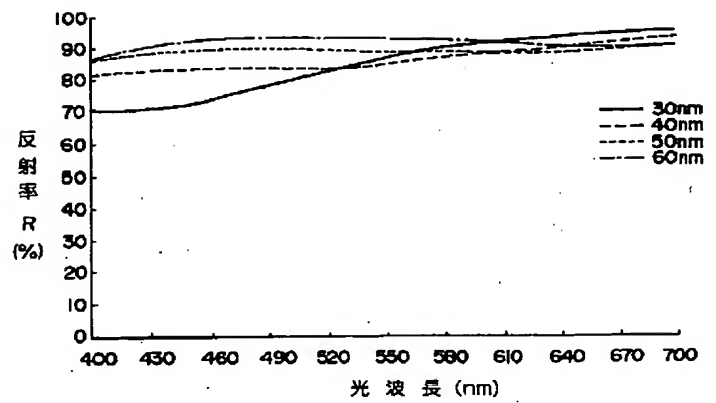
【図4】



【図5】

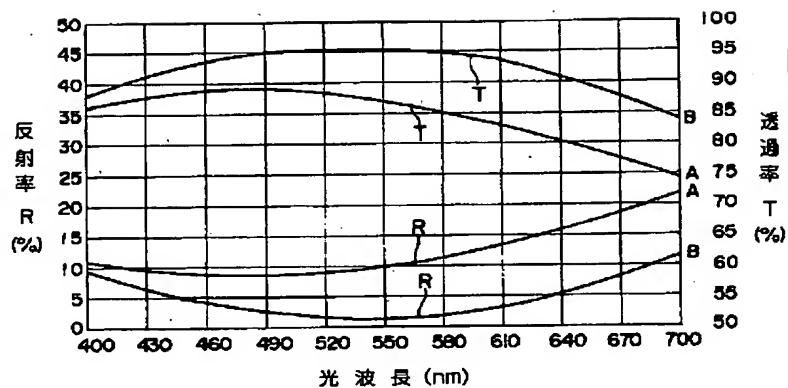


【図8】

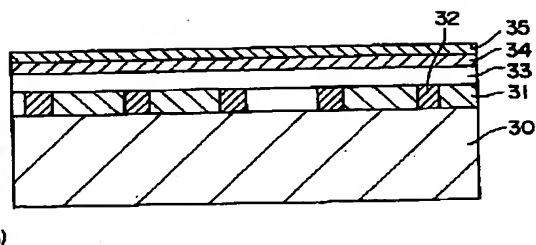


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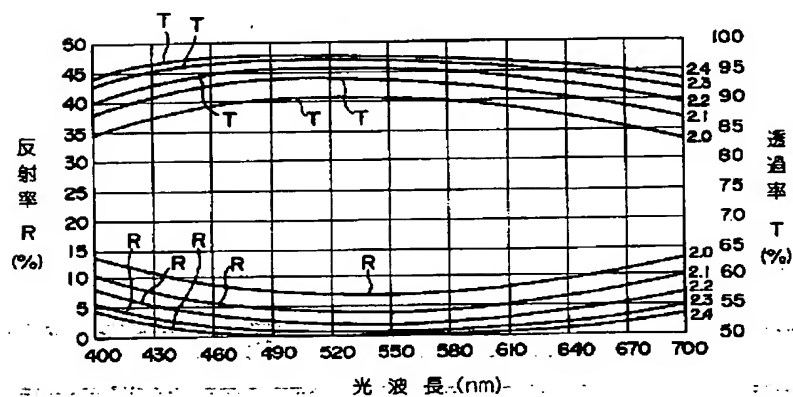
【図6】



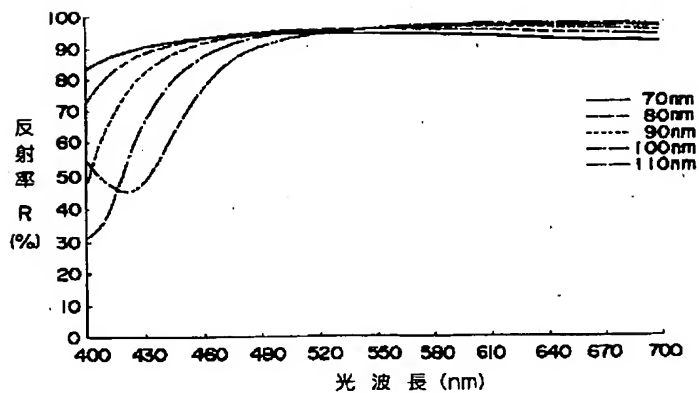
【図12】



【図7】

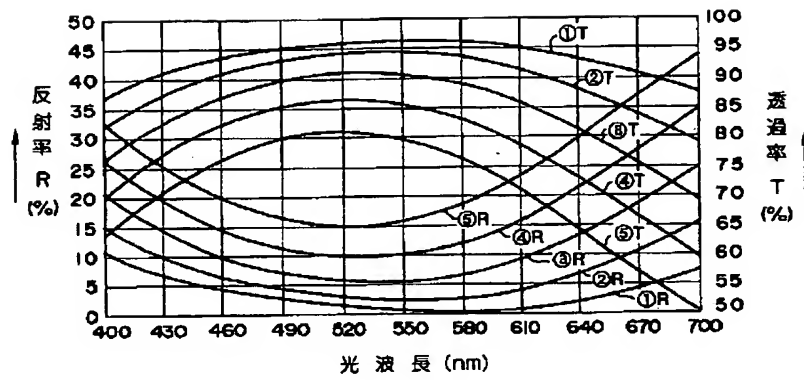


【図9】

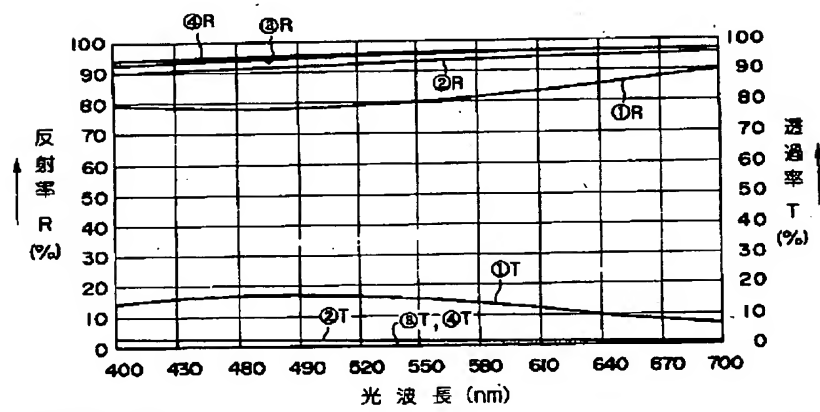


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【図10】



【図11】



フロントページの続き

(72)発明者 今吉 孝二
 東京都台東区台東1丁目5番1号 凸版印
 刷株式会社内

* NOTICES *

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2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

[Claim(s)]

[Claim 1] The electrode substrate for displays characterized by being formed in the electrode substrate which carries out the laminating of a conductive glue line, a silver system electric conduction thin film layer, and the oxide system transparence electric conduction thin film layer to this order with the silver alloy with which the silver system electric conduction thin film layer added a 0.1 - 2.5at% gold and 0.3 - 3.0at% copper, and forming the oxide system transparence electric conduction thin film layer with the amorphous matter on a substrate.

[Claim 2] The electrode substrate for displays according to claim 1 which is in within the limits whose thickness of said silver system electric conduction thin film layer is 50-200nm, and is in within the limits whose thickness of an oxide system transparence electric conduction thin film layer is 40-100nm.

[Claim 3] The electrode substrate for displays according to claim 1 with which it is in within the limits whose thickness of said silver system electric conduction thin film layer is 5-25nm, and said conductive glue line contains said oxide system transparence electric conduction thin film layer and an oxide of the same kind.

[Claim 4] The electrode substrate for displays according to claim 3 with which said conductive glue line and the whole oxide system transparence electric conduction thin film layer, or a part contains a larger oxide than a refractive index 2.1.

[Claim 5] The electrode substrate for displays according to claim 3 or 4 with which said conductive glue line and an oxide system transparence electric conduction thin film layer contain the oxide chosen from either or both among cerium oxide and titanium oxide.

[Claim 6] The electrode substrate for displays according to claim 3 to 5 with which said conductive glue line and an oxide system transparence electric conduction thin film layer contain indium oxide.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the electrode substrate of a transparency mold electrode

(transparent electrode) or a reflective mold electrode used for a display for I/O or a solar battery etc. which carries out a direct input from an output display unit or the display screens, such as liquid crystal display equipment and plasma display equipment, conductivity and light transmission of this invention are high at especially a thin film, and it relates to the electrode substrate which was moreover excellent in preservation stability.

[0002]

[Description of the Prior Art] The electrode plate with which the transparence electric conduction film of the electrode configuration which penetrates a visible ray was prepared on substrates, such as glass and plastic film, is widely used for the electrode for a display of various displays (display screen), such as liquid crystal display equipment, the I/O electrode which can carry out a direct input from the display screen of this display.

[0003] For example, the transparent electrode plate of the display unit with which liquid crystal was used The color filter layer 31 which is prepared in the pixel part on a glass substrate 30 and this glass substrate 30, and colors that transmitted light red, green, and blue for every pixel, respectively as shown in drawing 12, The light-shielding film 32 which is prepared in the part between the pixels on the above-mentioned glass substrate 30 (between pixels), and prevents the light transmission from this part, The transparent protection layer 33 prepared the whole surface on the above-mentioned color filter layer 31, Membranes are formed by sputtering on this protective layer 33, and that principal part consists of shape of a pattern etched into the predetermined electrode pattern, a solid transparent electrode 34, and orientation film 35 formed on this transparent electrode 34.

[0004] The ITO thin film which added tin oxide in indium oxide as this transparent electrode 34 paying attention to that high conductivity is used widely, that specific resistance is 2.4×10^{-4} ohm·cm about, and, in the case of the 240nm thickness usually applied as a transparent electrode, that sheet resistivity value is about 10ohms (or 10ohm/**, **; it is called a square). Moreover, although the tin oxide thin film, the thin film (Nesa membrane) constituted by tin oxide by adding antimony oxide or the thin film constituted by the zinc oxide by adding an aluminum oxide, etc. is known in addition to this, each of these is inferior to the above-mentioned ITO thin film in conductivity, and since chemical resistance or a water resisting property to an acid or alkali etc. is inadequate, generally they has not spread.

[0005] On the other hand, in the 7thICVM held in

Japan, the transparence electric conduction film of the three-tiered structure which the front rear face of a silver thin film is made to carry out the laminating of an ITO thin film or the indium oxide thin film (IO thin film) as heat ray reflective film, and is constituted is proposed in 1982. The transparence electric conduction film of this three-tiered structure has the low sheet resistivity value of about 5ohms, and the application to the above-mentioned transparent electrode was expected taking advantage of that high conductivity.

[0006]

[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned display unit or the I/O device, it is required that increasing a pixel consistency and displaying a precise screen in recent years should be called for, and the eburnation of the above-mentioned transparent electrode pattern should be demanded in connection with this, for example, the terminal area of the above-mentioned transparent electrode should be constituted from a pitch which is about 100 micrometers. Moreover, in the method (COG) with which direct continuation of the IC for a liquid crystal drive is carried out to a substrate in liquid crystal display equipment, there is a part from which leading about of wiring serves as a thin line called width of face of 20-50 micrometers, and the advanced etching processing suitability which is not in the former, and high conductivity (low resistance) are demanded.

[0007] Moreover, on the other hand, enlargement of the display screen was also called for, and in order to form the transparent electrode of a precise pattern which was mentioned above and to enable it to impress sufficient driver voltage for liquid crystal moreover about such large-sized screen-ization, the transparent electrode equipped with the high conductivity of the sheet resistivity value of 5ohms or less as the above-mentioned transparent electrode needed to be applied. moreover -- in addition, in the liquid crystal display of the passive-matrix drive method using STN LCD etc., when performing the multi-gradation display of 16 or more gradation, the low sheet resistivity value is demanded of the pan of 3ohms or less.

[0008] However, it also sets to the transparent electrode of the above-mentioned three-tiered structure proposed in the 7thICVM. By the sheet resistivity value of at most about 5ohms, not passing being obtained, but there being a trouble that sufficient conductivity is not securable, for example, thickening thickness of a silver thin film at about 16-18nm Even if it is possible to reduce the sheet resistivity value to about 3 ohms, visible-ray permeability (especially a long wave

with a wavelength of about 610nm visible-ray permeability by the side of merit) will fall to about 75%, and the function as a transparent electrode will be spoiled.

[0009] furthermore, the moisture in the air into which the silver thin film advanced from the laminating sea surface etc. in the transparent electrode of the above-mentioned three-tiered structure -- reacting -- easy -- the front face -- a reactant -- generating -- silverfish -- when the defect of a ** was produced, for example, it applied to the transparent electrode of a liquid crystal display, the trouble of being easy to produce a display defect etc. was shown in the front face.

[0010] Moreover, a polarizing plate is not used or the reflective mold liquid crystal display only by one polarizing plate (with liquid crystal displays, such as TN mold, a STN mold, an ECB mold, and an OCB mold, two polarizing plates are usually used) attracts attention in recent years.

[0011] In addition, development of the reflective mold liquid crystal display which arranged the reflective mold electrode which is made to have the reflecting plate of light and the function of a display electrode, and aimed at the cost cut in the liquid crystal cell is furthered.

[0012] this invention persons have proposed using the silver system thin film with the reflection factor of light covering the whole region mostly and higher than an aluminum thin film of a visible region as a reflector. In order to combine with the sulfur compound in air, for a sulfide to be generated by that front face, and for this silver system thin film to have the problem to which a reflection factor tends to fall and to prevent sulfuration of this silver system thin film, the approach of carrying out the laminating of the thin film of a transparence oxide on a silver system thin film is very effective.

[0013] However, when the laminating of the thin film of a transparence oxide was carried out on the silver system thin film, without taking optical conditions into consideration, the reflected light colored it yellow and pink and there was a problem on which the display grace of a reflective mold liquid crystal display is dropped greatly. Moreover, also in the reflector, like the transparent electrode of a three-tiered structure mentioned above, moisture resistance was low and leaving it also had the fault that silverfish occurred with moisture.

[0014] It is in offering the electrode substrate for displays of the transparency mold which this invention is made paying attention to such a trouble, and conductivity, visible-ray permeability, or whose reflection factor is [the place made into the technical problem] high at a thin film, moreover does not have degradation with the

passage of time, and was excellent in preservation stability, or a reflective mold.

[0015]

[Means for Solving the Problem] This invention is using two technique together as above-mentioned. The means for solving a technical problem, and it is one of them adding a small amount of gold and copper to silver of a silver system thin film, and being suppressing silver description, and another's making the thin film of a transparence oxide amorphous, and losing silver grain boundary diffusion (silver's tending to cause the grain boundary diffusion during the crystal of an oxide).

[0016] Namely, invention concerning claim 1 of this invention is set to the electrode substrate in which this order carries out the laminating of a conductive glue line, a silver system electric conduction thin film layer, and the oxide system transparence electric conduction thin film layer on a substrate. It is the electrode substrate for displays characterized by being formed with the silver alloy with which the silver system electric conduction thin film layer added a 0.1 - 2.5at% gold and 0.3 - 3.0at% copper, and forming the oxide system transparence electric conduction thin film layer with the amorphous matter.

[0017] Moreover, invention concerning claim 2 is an electrode substrate for displays which is in within the limits whose thickness of said silver system electric conduction thin film layer is 50-200nm, and is in within the limits whose thickness of an oxide system transparence electric conduction thin film layer is 40-100nm in the electrode substrate for displays of the above-mentioned invention.

[0018] Moreover, in the electrode substrate for displays of the above-mentioned invention, within the limits whose thickness of said silver system electric conduction thin film layer is 5-25nm has invention concerning claim 3, and said conductive glue lines are said oxide system transparence electric conduction thin film layer and an electrode substrate for displays containing an oxide of the same kind.

[0019] Moreover, invention concerning claim 4 is an electrode substrate for displays with which said conductive glue line and the whole oxide system transparence electric conduction thin film layer, or a part contains a larger oxide than a refractive index 2.1 in the electrode substrate for displays of the above-mentioned invention.

[0020] Moreover, invention concerning claim 5 is an electrode substrate for displays with which said conductive glue line and an oxide system transparence electric conduction thin film layer contain the oxide chosen from either or both among cerium oxide and titanium oxide in the electrode substrate for displays of the

above-mentioned invention.

[0021] Moreover, invention concerning claim 6 is an electrode substrate for displays with which said conductive glue line and an oxide system transparence electric conduction thin film layer contain indium oxide in the electrode substrate for displays of the above-mentioned invention.

[0022]

[Embodiment of the Invention] Invention concerning claim 1 of this invention is explained below at a detail according to the gestalt of operation.

[0023] In the electrode substrate with which this order carries out the laminating of a conductive glue line, a silver system electric conduction thin film layer, and the oxide system transparence electric conduction thin film layer on a substrate in invention concerning claim 1 of this invention a silver system electric conduction thin film layer -- 0.1 - 2.5at% (following atomic weight% --) It is the electrode substrate for displays in which it is formed in with the silver alloy which added the gold which calls atomic-weight percent at%, and 0.3 - 3.0at% copper, and the oxide system transparence electric conduction thin film layer is formed with the amorphous matter.

[0024] The addition of the gold to the above-mentioned silver system electric conduction thin film layer on the above-mentioned substrate has the inclination for moisture resistance to improve as it is effective from 0.1at% of little addition and makes [many] this addition about the improvement in moisture resistance respectively of the conductive glue line which is the electric conduction film of a three-tiered structure, a silver system electric conduction thin film layer, and an oxide system transparence electric conduction thin film layer.

[0025] However, since remnants will become easy to remain at the time of etching processing of the electric conduction film if the resistance as electric conduction film will rise if a golden addition increases, and it carries out to more than 2.5at%, a proper addition needs to be adjusted.

[0026] As described above, while addition of the copper to a silver system electric conduction thin film layer contributes to damp-proof improvement, only silver (Ag) by two elements of Ag-Au(gold) Although it is easy to produce fluctuation in membrane formation thickness, the permeability after membrane formation, etc. in response to the effect of the oxygen in the gas ambient atmosphere at the time of sputtering membrane formation There is effect which a depression will be lost if copper (Cu) is added, therefore stops being influenced of an ambient atmosphere easily, and extends the margin at the time of membrane formation of a silver system electric conduction

thin film layer (permissible doses, such as membrane formation conditions) especially.

[0027] If oxygen exists in the introductory gas or the background at the time of membrane formation of a silver system electric conduction thin film layer mostly, light absorption will arise near the wavelength of 470nm, and, specifically, decline in the light transmittance (a reflective mold electrode reflection factor) as a transparent electrode will arise.

[0028] The transparent silver system electric conduction thin film layer in which drawing 5 was formed with the silver alloy with which the silver system electric conduction thin film layer added a 0.1 - 2.5at% gold and 0at% - 3.0at% copper, It is the graph which shows the spectral transmittance of the transparent electrode substrate for displays of the three-tiered structure formed of the oxide system transparence electric conduction thin film layer by the amorphous matter (the total thickness of the electric conduction film of a three-tiered structure; in the case of about 85nm). In copper 0at% addition, graph ** graph ** In the case of copper 0.3at% addition In copper 1.0at% addition, graph ** of graph ** is the case of copper 3.0at% addition, the depressions by the side of short wavelength decrease in number gradually from about 0.3%, and the addition of the copper to the above-mentioned silver system electric conduction thin film layer is effective in raising depression of the permeability by the side of short wavelength, as shown in above-mentioned drawing 5.

[0029] In order that copper may take the form (it is not full dissolution) of an eutectic to silver, when ~~it will come to have bad effect on light transmittance~~ or a reflection factor if a copper addition increases and an addition increases, it has the inclination for the resistance of the electric conduction film to rise.

[0030] For example, when thickness of the above-mentioned silver system electric conduction thin film layer is set to 10-11nm and a copper addition is made more than 3at%, a sheet resistivity value comes to exceed 5 ohms.

[0031] In order to make amorphous the above-mentioned oxide system transparence electric conduction thin film layer, it is simple to set up substrate temperature low by the forming-membranes methods, such as sputtering, and to make it amorphous (for example, 20 degrees C or less or a room temperature etc.) using the oxide target which carries out considerable amount (it is generally 20% or more although it changes with compatibility of oxide) mixing of the dissimilar metal, to a certain kind of metallic oxide.

[0032] Moreover, what is necessary is just to select

from the ingredient which is rich in acid resistance, alkali resistance, and thermal resistance as the above-mentioned metallic oxide.

[0033] Next, the conductive glue line according to the electric conduction thin film of an oxide system to a glass substrate top on the assumption that the application of a reflector (for example, wavelength dispersion, such as 10nm of thickness, a refractive index 2.3 however a refractive index by light wave length, and change of an absorption coefficient, was disregarded), Simulation of the display electrode substrate of the reflective mold which carried out the laminating of 50nm - 200nm of silver system electric conduction thin film layers and the oxide system transparence electric conduction thin film layer (40nm of for example, thickness) one by one was performed.

[0034] And the simulation result of the reflection factor of the electric conduction thin film layer of the display electrode substrate of the above-mentioned reflective mold is shown in drawing 11. As for 75nm of thickness of a silver system electric conduction thin film, and graph **, graph ** shows the case of 200nm of thickness of a silver system electric conduction thin film for 50nm of thickness of a silver system electric conduction thin film, and graph **, as for 100nm of thickness of a silver system electric conduction thin film, and graph **. In addition, the refractive index of the measurement medium (medium which intervenes in the path of a measuring beam) to be used was set to 1.5.

[0035] Next, invention concerning claim 2 of this invention is explained below at a detail according to the gestalt of operation.

~~[0036] Invention concerning claim 2 is an electrode substrate for displays which is in within the limits whose thickness of said silver system electric conduction thin film layer is 50-200nm, and is in within the limits whose thickness of an oxide system transparence electric conduction thin film layer is 40-100nm in the electrode substrate for displays of invention of above-mentioned claim 1.~~

[0037] That is, the range whose thickness of the silver system electric conduction thin film layer as a reflecting layer is 50nm - 200nm has invention concerning claim 2 on the assumption that the application of a reflective mold display electrode substrate, and it is in the range whose thickness of an oxide system transparence electric conduction thin film layer is 40nm - 100nm.

[0038] Drawing 11 will serve as a reflective mold electrode before and behind 80% of reflection factors, if the thickness of a silver system electric conduction thin film layer exceeds 50nm, although the effect to the reflection factor of the thickness of a silver system electric conduction thin film layer

is shown, a reflection factor is saturated with 200nm, and it is shown that light transmittance becomes about 0%.

[0039] In drawing 8 and drawing 9, the simulation result in a reflective mold electrode of having taken the wavelength dispersion into consideration about the relation between the thickness of a silver system electric conduction thin film layer and a reflection factor was shown, and the optical constant (a refractive index, extinction coefficient of light) was respectively shown in Table 1 at them about the silver system electric conduction thin film layer (AgAuCu) and the oxide system electric conduction thin film layer (ICTTO).

[0040]

[Table 1]

波長 (nm)	AgAuCu		ICTTO	
	屈折率	消衰係数	屈折率	消衰係数
400	0.1730	1.9500	2.4986	0.0444
410	0.1729	2.0714	2.4736	0.0347
420	0.1666	2.1820	2.4510	0.0275
430	0.1594	2.2835	2.4304	0.0220
440	0.1575	2.3750	2.4116	0.0178
450	0.1510	2.4715	2.3944	0.0145
460	0.1434	2.5674	2.3787	0.0120
470	0.1365	2.6588	2.3643	0.0099
480	0.1316	2.7467	2.3510	0.0083
490	0.1306	2.8313	2.3387	0.0070
500	0.1300	2.9186	2.3274	0.0059
510	0.1299	3.0107	2.3169	0.0051
520	0.1298	3.0979	2.3072	0.0044
530	0.1293	3.1784	2.2981	0.0038
540	0.1286	3.2576	2.2897	0.0033
550	0.1248	3.3404	2.2818	0.0029
560	0.1212	3.4213	2.2745	0.0025
570	0.1202	3.5013	2.2676	0.0022
580	0.1206	3.5800	2.2612	0.0020
590	0.1210	3.6570	2.2551	0.0017
600	0.1243	3.7330	2.2495	0.0016
610	0.1277	3.8076	2.2441	0.0014
620	0.1310	3.8809	2.2391	0.0013
630	0.1338	3.9654	2.2344	0.0011
640	0.1366	4.0481	2.2299	0.0010
650	0.1393	4.1292	2.2256	0.0009
660	0.1400	4.2109	2.2216	0.0008
670	0.1399	4.2918	2.2178	0.0008
680	0.1399	4.3713	2.2142	0.0007
690	0.1402	4.4492	2.2108	0.0006
700	0.1423	4.5250	2.2076	0.0006

[0041] It is shown that the thickness of the above-mentioned oxide system transparence electric conduction thin film layer becomes [the reflection factor of 435nm (blue dominant wavelength)] as low as about 70% by 30nm or less

and 110nm or more.

[0042] Moreover, it is shown that the thickness of an oxide system transparence electric conduction thin film layer has a reflection factor good in 40nm - 100nm.

[0043] Next, invention concerning claim 3 of this invention is explained below at a detail according to the gestalt of operation.

[0044] In the electrode substrate for displays of invention concerning above-mentioned claim 1, within the limits whose thickness of said silver system electric conduction thin film layer is 5-25nm has invention concerning claim 3, and said conductive glue lines are said oxide system transparence electric conduction thin film layer and an electrode substrate for displays containing an oxide of the same kind.

[0045] The simulation of the spectral transmittance by the display electrode substrate of the transparency mold which carried out the laminating of the conductive glue line (for example, 35nm of thickness, a refractive index 2.2) by the transparence electric conduction thin film of an oxide system, and 15nm - 25nm of silver system electric conduction thin film layers and an oxide system transparence electric conduction thin film layer (40nm of for example, thickness) to drawing 10 one by one on the glass substrate the premise [the application of a transparency mold electrode] was shown. For 15nm of thickness of a silver system electric conduction thin film layer, and graph **, 17.5nm of thickness of a silver system electric conduction thin film layer and graph ** are [graph ** / 22.5nm of thickness of a silver system electric conduction thin film layer and ** of 20.0nm of thickness of a silver system electric conduction thin film layer and graph **] the cases of 25.0nm of thickness of a silver system electric conduction thin film layer, and the measurement medium was made into the refractive index 1 as Ayr (air).

[0046] Also in the comparatively thick field whose thickness of a silver system electric conduction thin film layer is 25nm, 80% with the comparatively good permeability of a peak is obtained. Moreover, the sheet resistivity value of the electric conduction film of a three-tiered structure is set to about 2 ohms by the thickness of a silver system electric conduction thin film layer by a little more than 20nm.

[0047] Moreover, in less than 5nm of thickness, it becomes island-like (the shape of a land), and it does not become the homogeneous film, it becomes difficult to compute the proper optical property and proper resistance on count, and a silver system electric conduction thin film layer does not serve as good electric conduction film of three layers in the field of the ultra-thin film of 5nm or

less of thickness.

[0048] In addition, the electric conduction film of the three-tiered structure on condition of the display electrode substrate of a transparency mold has effect with the sufficient direction to permeability and resistance by which the laminating is carried out to front flesh-side both-sides side of a silver system electric conduction thin film layer and which the membrane formation conditions (for example, the conditions at the time of membrane formation, oxygen tension, etc.) of an oxide system transparency electric conduction thin film layer approximate more mutually, respectively.

[0049] moreover, each by the side of front flesh-side both sides of a silver system electric conduction thin film layer -- if the membrane formation ingredient of the aforementioned oxide system transparency electric conduction thin film layer is the same, material controls, such as a target for sputtering membrane formation, are also easy.

[0050] By the way, the technical progress of the liquid crystal display display of passive matrices, such as STN and ECB, has a motion that it is remarkable and a color STN method will be used as a monitor of a CRT alternative, when it is a deferred monitor, connection with external powers, such as 100V and 110V, is possible for it, and the daily use of the back light of high brightness of it is attained from such a thing in recent years.

[0051] Although priority will be given to the transparent electrode used for this being low resistance in the liquid crystal display display of the passive matrix of a monitor application from this viewpoint and permeability may be made to some extent into a sacrifice. If the effect of the resistance of a transparent electrode is very large and the sheet resistivity value of the transparent electrode mentioned above becomes near 2ohm, since deterioration of the image quality called shadowing will almost be lost for the improvement in image quality in such a passive matrix, It can compete with a TFT method on practical use level as a display.

[0052] Next, invention concerning claim 4 of this invention is explained below at a detail according to the gestalt of operation.

[0053] Invention concerning claim 4 is an electrode substrate for displays with which said conductive glue line and the whole oxide system transparency electric conduction thin film layer, or a part contains a larger oxide than a refractive index 2.1 in the electrode substrate for displays of invention concerning above-mentioned claim 3.

[0054] When this invention persons repeated examination further, they found out that the configuration of the electric conduction film of the

three-tiered structure which used the oxide with a larger refractive index than 2.1 for the oxide system transparency electric conduction thin film layer obtained a still better result as mentioned above.

[0055] And it found out that effectiveness was in improvement in light transmittance by inserting an oxide with a high refractive index (an oxide being practical in respect of a manufacturing cost etc., although it does not limit to an oxide, if transparent in a light field) in a glue line, the whole oxide system transparency electric conduction thin film layer, or these parts.

[0056] In the case of a liquid crystal ingredient (the refractive index of the usual liquid crystal is 1.5 to about 1.6) with a refractive index higher than Ayr (air), and the electric conduction film of the three-tiered structure for the liquid crystal display of the gestalt which touches a color filter (extent to which the refractive index of the ingredient of a color filter exceeds 1.5 a little), the rise of the light transmittance using a high refractive-index ingredient is remarkable.

[0057] For example, although B line of drawing 6 shows a simulation result in case one side of the display electrode of the transparency mold of the three-tiered structure formed on substrates, such as glass, is Ayr (air), in permeability T, a reflection factor R falls about 96% at a peak till the place near 1%, and a result good as a display electrode substrate (transparent electrode) of a transparency mold is obtained.

[0058] Here, thickness of the oxide system transparency electric conduction thin film layer (transparency oxide thin film) of the side which touches the thickness L of the glue line by the transparency oxide thin film by the side of a substrate is 14nm and air in the thickness of 40nm and a transparent silver system electric conduction thin film layer (Ag thin film) was set to 44nm. And the refractive index of these transparency oxide thin film was computed as the 2.0 [almost same] as ITO.

[0059] However, 40nm laminating of the orientation film of polyimide is carried out on the above-mentioned transparent electrode of a three-tiered structure, if the refractive index of the liquid crystal which touches this is computed as 1.5, as A line of drawing 6 shows, in permeability T, a peak will fall to 90% or less, a reflection factor R will rise to about 10% near 550nm of light wave length, and the engine performance as a display electrode substrate (transparent electrode) of a transparency mold will fall.

[0060] each which pinches this invention persons' silver system electric conduction thin film layer for count in the form where the polyimide film and

liquid crystal as orientation film of liquid crystal touch the display electrode substrate of the transparency mold of a three-tiered structure from this, on the front reverse side -- it carried out by changing and optimizing the each refractive index of a transparent oxide thin film (also adjusting thickness at the same time it changes a refractive index).

[0061] The result is shown in drawing 6. This drawing shows that the higher one of permeability improves to extent to which especially the refractive index of a transparency oxide thin film exceeds 2.1, and a reflection factor also falls.

[0062] Next, invention concerning claim 5 of this invention is explained below at a detail according to the gestalt of operation.

[0063] Invention concerning claim 5 is an electrode substrate for displays with which said conductive glue line and an oxide system transparency electric conduction thin film layer contain the oxide chosen from either or both among cerium oxide and titanium oxide in the electrode substrate for displays of invention concerning above-mentioned claim 3 or claim 4.

[0064] When premised on the display electrode substrate (transparent electrode) of a transparency mold, permeability is made to improve by using for the transparency oxide thin film used for this invention, and using a high refractive-index ingredient as an ingredient.

[0065] The typical oxide of this high refractive-index ingredient is cerium oxide and titanium oxide, and raises the light transmittance of the electric conduction film of the three-tiered structure as a transparent electrode by mixing

these with different-species oxide at about 20 - 80% of a rate, and forming a transparent conductive glue line and an oxide system transparency electric conduction thin film layer.

[0066] Next, invention concerning claim 6 of this invention is explained below at a detail according to the gestalt of operation.

[0067] Invention concerning claim 6 is an electrode substrate for displays with which said conductive glue line and an oxide system transparency electric conduction thin film layer contain indium oxide in the electrode substrate for displays of invention concerning above-mentioned claim 3, claim 4, or claim 5.

[0068] In the electrode substrate for displays of this invention, it is necessary to take an electric flow from the front face of a transparency oxide thin film for the drive of a display device.

[0069] Moreover, in order to make a transparency oxide thin film make it amorphous in the form (for example, form where crystallization does not progress in annealing near 250 degree C) stabilized comparatively also thermally, as

described above, it is necessary to make it the mixed oxide thin film of different-species oxide addition in about 20 - 80% of range.

[0070] There was little oxide which can take an electric flow in the state of such an amorphous mixed oxide, and it found out that it was advantageous to make the ingredient of a transparency oxide thin film into indium oxide in the range which this invention persons examined.

[0071] What is necessary is just to still more specifically form membranes by the membrane formation approaches, such as sputtering, using the oxide target which made cerium oxide (or titanium oxide) mix with indium oxide in about 20 - 80% of range. In addition, if a mixed rate is amorphous as a transparency oxide thin film even if it does not go into the above-mentioned range, it is good.

[0072] Although the electrode substrate for displays of this invention includes all of the electrode substrate for displays of a transparency mold or a reflective mold, when it is the electrode substrate for displays of a reflective mold, the substrate to be used may be the transparency or the opaque substrate colored the color of transparent substrates, such as glass and plastics, or white, black, and others, for example. And the ingredient of a substrate can also use various things, such as a substrate with which semiconductor devices, such as glass, plastic film, a sheet plastic, a ceramic, a metal plate or an amorphous silicon, polish recon, and MIM, were formed. Moreover, pattern formation of the color filter layer (for example, red, Green, each blue coloring layer) may be beforehand carried out to said substrate to be used.

[0073] Moreover, since the electric conduction film of the three-tiered structure of this invention is low resistance, it is also possible to be able to use it for signal lines, bus lines, etc. of a component, such as TFT and MIM, and to use also [electrodes / these / pixel].

[0074]

[Example] The concrete example of this invention is shown below.

[0075] As shown in <example 1> drawing 1, the electrode substrate 15 for displays of the transparency mold concerning this example The transparency oxide thin film 11 (oxide system transparency electric conduction thin film layer) which is a conductive glue line with a thickness of 35nm by which the laminating was carried out one by one on the glass substrate 10 with a thickness of 0.7mm, The principal part consists of a transparent silver system electric conduction thin film 12 (silver system electric conduction thin film layer) with a thickness of 14nm and a transparency oxide thin film 13 (oxide system

transparence electric conduction thin film layer) with a thickness of 38nm. in addition, the above-mentioned transparence oxide thin films 11 and 13 -- the any -- although -- cerium oxide (it is 32at(s)% by the métallic element conversion except oxygen) was used as the mixed oxide added to the thin film of indium oxide. Moreover, the above-mentioned transparence oxide thin film 11 and the silver system thin film 12 between 13 are the silver alloys which added golden 1.0at% and copper 1.5at% to silver.

[0076] And the transparence electric conduction film 14 of the above-mentioned three-tiered structure formed membranes by the following approaches. First, after the surfactant and water of an organic alkali system washed the front face of a glass substrate 10, it held in the vacuum tub, plasma treatment called reverse sputtering was performed, and washing processing of the front face was carried out further.

[0077] Next, without taking out a glass substrate 10 out of a vacuum tub, where this glass substrate 10 is maintained to a room temperature, laminating membrane formation of the transparence oxide thin film 11, the silver thin film 12, and the transparence oxide thin film 13 was carried out one by one by the sputtering method.

[0078] Next, pattern formation of the resist film of an electrode configuration was carried out by the photolithography method on the transparence oxide thin film 13, the part exposed from this resist film was etched with the nitric-acid system etching reagent, where location adjustment of the thin film of the above-mentioned three-tiered structure is carried out mutually, patterning was carried out to the electrode configuration, then 220 degrees C and annealing treatment of 1 hour were performed, the above-mentioned transparent electrode 14 of an electrode configuration was formed, and the electrode substrate 15 for displays of a transparency mold was produced. In this way, the sheet resistivity value of the obtained transparent electrode 14 was about 3.3ohms.

[0079] A continuous line shows the visible-ray permeability (graph **) of the transparent electrode 14 of the example 1 which gave the silver system electric conduction thin film layer of the 14nm of the above-mentioned thickness to drawing 4 . In addition, the permeability of the transparent electrode 14 (sheet resistivity value; about 4.6ohms) with which graph ** gave the silver system electric conduction thin film layer of 12nm or less of thickness, and graph ** show the permeability of the transparent electrode 14 (thickness:nm [about 90], sheet resistivity value; about 2.2ohms) which gave the silver system electric conduction thin film layer of, 19nm of

thickness.

[0080] After holding this transparent electrode 14 that carried out pattern formation in 60 degrees C and the ambient atmosphere of 95% of humidity for 500 hours, that front face was observed. Consequently, the front face did not produce appearance change at all. In addition, it was 2.24 when the refractive index of the transparent electrode 14 by this mixed oxide was measured.

[0081] Although the peak of the minute silver by the silver thin film 12 was observed in this transparent electrode 14 when that crystallinity was investigated by the thin film X diffraction, the peak of the crystal by the transparence oxide thin films 11 and 13 was not observed.

[0082] And even if the above-mentioned transparent electrode 14 was thermally stable and having been heat-treated to 300 degrees C, the peak of a crystal was not observed by the transparence oxide thin film, and most rises of the sheet resistivity value were not looked at.

[0083] As shown in <example 2> drawing 2 , the electrode substrate 25 for displays of the reflective mold concerning this example The oxide thin film 21 (transparence thru/or opaque oxide thin film) with a thickness of 10nm which is the conductive glue line by which the laminating was carried out one by one on the glass substrate 20 with a thickness of 0.5mm, The principal part consists of a silver system thin film 22 (silver system electric conduction thin film layer) with a thickness of 150nm and a transparence oxide thin film 23 (oxide system transparence electric conduction thin film layer) with a thickness of 75nm.

[0084] The above-mentioned transparence oxide thin films --21-- and --23-- considered respectively indium oxide, cerium oxide, tin oxide, and titanium oxide as titanium 0.5at% of presentation tin 1.0at% cerium 32.5at% indium 66at% at the atomic percent of only the metal atom which does not include an oxygen atom in a number. The sheet resistivity value of the reflective electric conduction film 24 of these three-tiered structures was about 0.2ohms.

[0085] Although the spectral characteristic of this reflective type of electrode substrate 25 for displays was shown in drawing 3 , by 450nm - 700nm, about 90% or more of high reflection factor was obtained 80% by 400nm.

[0086] And the reflective electric conduction film 24 of the above-mentioned three-tiered structure formed membranes by the following approaches. First, after the surfactant and water of an organic alkali system washed the front face of a glass substrate 20, it held in the vacuum tub, plasma treatment called reverse sputtering was performed, and washing processing of the front face was carried out further.

[0087] Next, without taking out a glass substrate 20 out of a vacuum tub, where this glass substrate 20 is maintained to a room temperature, laminating membrane formation of the transparency oxide thin film 21, the silver thin film 22, and the transparency oxide thin film 23 was carried out one by one by the sputtering method.

[0088] Next, carry out pattern formation of the resist film of an electrode configuration by the photolithography method on the transparency oxide thin film 23, and the part exposed from this resist film is etched with a nitric acid system etching reagent. Where location adjustment of the thin film of the above-mentioned three-tiered structure is carried out mutually, patterning was carried out to the electrode configuration, then 220 degrees C and annealing treatment of 1 hour were performed, the above-mentioned reflective electric conduction film 24 of an electrode configuration was formed, and the electrode substrate 25 for displays of a reflective mold was produced. In this way, the sheet resistivity value of the obtained reflective electric conduction film 24 was about 0.2ohms.

[0089] Although the crystal peak of the silver by the silver thin film 22 was observed in the reflective electric conduction film 24 when crystallinity was investigated by the thin film X diffraction, the peak of the crystal by the transparency oxide thin films 21 and 23 was not observed.

[0090] Even if the reflective electric conduction film 24 was thermally stable and having been heat-treated to 300 degrees C, the peak of the crystal by the transparency oxide thin films 21 and 23 was not observed. Moreover, as a result of holding in 60 degrees C and the ambient atmosphere of 95% of humidity for 500 hours and observing the front face, there was also no appearance change and moisture resistance was high.

[0091]

[Effect of the Invention] The electrode substrate for displays of this invention by using for a silver system thin film a small amount of gold to silver, and the silver alloy which added copper. Moreover, by being able to give moisture resistance to the electrode substrate for displays, and there being effectiveness which makes dependability high, and using the with a refractive indexes of 2.1 or more transparency oxide thin film of a high refractive index by making a transparency oxide thin film amorphous at coincidence. While it is effective in the electrode substrate for displays of the high transparency mold of permeability being obtained, and continuing throughout the wavelength of the light and the electrode

substrate for displays of the high reflective mold of a reflection factor being obtained, and being low resistance in a thin film and showing good conductivity. There is practical effectiveness as an electrode substrate for displays of the transparency mold which visible-ray permeability or whose reflection factor is high, moreover does not have degradation with the passage of time, and was excellent in preservation stability, or a reflective mold.

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